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SPECIFICATION

TO ALL WHOM IT MAY CONCERN:

BE IT KNOWN THAT WE, Koji Nozaki, a citizen of Japan residing at Kawasaki-shi, Kanagawa, Japan and Ei Yano, a citizen of Japan residing at Kawasaki-shi, Kanagawa, Japan have invented certain new and useful improvements in

POLYMER COMPOUND FOR A CHEMICAL AMPLIFICATION RESIST AND A FABIRCATION PROCESS OF A SEMICONDUCTOR DEVICE USING SUCH A CHEMICAL AMPLIFICATION RESIST

of which the following is a specification : -

1 TITLE OF THE INVENTION

POLYMER COMPOUND FOR A CHEMICAL
AMPLIFICATION RESIST AND A FABRICATION PROCESS OF A
SEMICONDUCTOR DEVICE USING SUCH A CHEMICAL

5 AMPLIFICATION RESIST

BACKGROUND OF THE INVENTION

The present invention generally relates to a resist composition that can be developed by a basic 10 developing liquid and a fabrication process of a semiconductor device using such a resist composition.

With the advancement in the art of device miniaturization, recent semiconductor integrated circuits designated as LSIs or VLSIs are now patterned 15 with sub-micron line widths. Further, intensive investigations are being made on so-called sub-halfmicron devices that use a minimum pattern width of smaller than 0.5 μm .

In order to fabricate such sub-halfmicron 20 devices, it is essential to reduce the wavelength of the optical radiation that is used for exposing a pattern on a semiconductor substrate, from a conventional, normal ultraviolet wavelength to a far-ultraviolet wavelength. Further, investigations are 25 being made also on the exposure process that uses a deep ultraviolet wavelength radiation. Associated with such a shift in the wavelength of the optical radiation used for photolithography, there is an urgent demand for a resist composition that shows a 30 reduced optical absorption in such a very short wavelength band and simultaneously a high dry etching resistance and a high sensitivity.

In recent years, intensive studies have been 35 made on the photolithography that uses a novel optical source of KrF excimer laser. A KrF excimer laser produces an optical radiation with a wavelength of 248 nm, and the technology of the KrF excimer laser

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1 photolithography is now being reduced to practice. In
relation to the development of photolithography that
uses such a very short wavelength optical radiation,
there is proposed a concept of chemical amplification
5 resist (J.M.J. Frechet, et al., Proc. Microcircuit
Eng., 260 (1982), H. Ito, et al., Digest of Technical
Papers of 1982 Symposium on VLSI Technology, 86
(1983), H. Ito, et a., "Polymer in Electronics," ACS
Symposium Series 242, T. Davidson ed., ACS, 11 (1984),
10 United States Patent 4, 491, 628) that shows a high
sensitivity and high resolution in the exposure
process conducted by such very short wavelength
optical radiations.

The basic concept of chemical amplification
15 resist is to increase the apparent quantum yield by
inducing a catalytic reaction in the resist film.

In the example of widely studied, as well as
widely used, chemical amplification positive type
resist, in which a PAG (photo acid generator) is added
20 to t-butoxycarbonyl (t-BOC) polyvinyl phenol (PVP),
the t-BOC group functions as a protective group and
causes a desorption as a result of the post exposure
baking (PEB) process conducted after the exposure. As
a result of the PEB process, isobutene and carbon
25 dioxide are formed. As such a desorption process
releases a protonic acid, a chain reaction is
triggered in the resist composition with regard to the
deblocking reaction, and the polarity of the resist is
changed significantly in the exposed part of the
30 resist film. Thus, by applying a suitable developing
liquid to the resist film thus exposed, a resist
pattern is successfully formed.

On the other hand, recent attempts of
forming semiconductor devices of still higher
35 integration density such as Gbit DRAMs, have urged an
investigation on the photolithography that uses a
still shorter wavelength optical radiation of 193 nm

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1 wavelength band produced by an ArF excimer laser. In
the photolithographic process that uses such a very
short wavelength optical radiation, the problem of
strong optical absorption by the resist is inevitable
5 as long as a phenolic polymer resin is used for the
resist base. Thus, there is an urgent demand for a
resist that is applicable to such a very short-
wavelength optical radiation.

While there are various chemical
10 amplification resists studied for application to an
exposure process conducted with the optical radiation
of 193 nm wavelength, most of the conventionally
studied resists are based on a methacrylic resin that
has an ester group called polycyclic alicyclic group.
15 Examples thereof are adamantane, isobornane,
tricyclodecane, and others. See for example, Nozaki,
K., et al, Chem. Mater., 1994, 6, 1492-1498, Nakano,
K., et al, Proc. SPIE, 1994, 2195, 194-204, and Allen,
R. D., et al, Proc. SPIE, 1994, 2438, 474-485. The
20 foregoing conventional resists successfully realize
the necessary dry-etching resistance that is essential
for a resist, by incorporating alicyclic ester group
into the base resin.

On the other hand, the foregoing
25 conventional resists have suffered from the problems,
associated with the use of the alicyclic group in the
resin, such as a peeling-off of the resist during the
developing process or an insufficient dissolving of
the exposed area to an alkaline developer. In order
30 to overcome the foregoing problems, there are
proposals such as incorporation of carboxylic acid
unit into the base resin or using a diluted developing
liquid. Further, there are proposals for mixing an
alcohol such as isopropyl alcohol to the developer.

35 Further, there is a report of a chemical
amplification resist composition that solves the
foregoing problems successfully (Nozaki, K., et al.,

DEPARTMENT OF DEFENSE

1 Jpn. J. Appl. Phys., 35, 1996, L528-L530). The
reported resist uses mevalonic lactone and
2-methyl-2-adamantanol for the protective group of the
carboxylic acid in the base resin.

5 In the foregoing resist composition, both of
the protective groups cause deprotection, while such
deprotection enables a development of the resist by
using a standard alkaline developer. As mevalonic
10 lactone has a strong polarity, the resist composition
shows an improved adhesion to a substrate. Further,
the resist composition has a sufficient sensitivity
and enables formation of ultra-fine patterns without
swelling.

On the other hand, there has been a problem
15 in the foregoing conventional resist composition in
that the synthesis of mevalonic lactone methacrylate
has to be conducted at a low temperature, and that the
mevalonic lactone source material is expensive.

20 SUMMARY OF THE INVENTION

Accordingly, it is a general object of the
present invention to provide a novel and useful resist
composition wherein the foregoing problems are
eliminated.

25 Another and more specific object of the
present invention is to provide a novel and useful
acid-sensitive polymer for a resist composition that
has a practical sensitivity to a deep-ultraviolet
optical radiation and forms an ultra-fine pattern free
30 from swelling or peeling-off after a development
process conducted by a standard alkaline developer.

Another object of the present invention is
to provide a novel resist composition that is
sensitive to a deep-ultraviolet radiation produced by
35 a KrF excimer laser or an ArF excimer laser and
simultaneously has an excellent dry-etching
resistance.

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1 Another object of the present invention is
to provide a novel resist composition capable of
forming ultra-fine patterns with high sensitivity,
sharp contrast and high resolution, by realizing a
5 large difference of polarity between an exposed area
and an unexposed area of the resist composition.

Another object of the present invention is
to provide a method of forming a resist pattern by
using such a resist composition as well as a
10 fabrication method of a semiconductor device using
such a resist pattern.

In an investigation conducted by the
inventors of the present invention and now forming the
basis of the present invention, it has been discovered
15 that it is important to use a film-forming polymer
that includes a carboxyl group in a side chain of a
monomer unit forming a part of the polymer as the base
resin of the chemical amplification resist, and that
the carboxyl group includes a compound having a
20 specific lactone part as a protective group. Further,
it has been discovered that it is important that the
film-forming polymer contains an additional acidic
functional group that has an acid-cleavable protective
group in a side chain of the resin.

25 In a first aspect of the present invention,
there is provided a resist composition insoluble to a
basic solution but becoming soluble after an exposure
process to an optical radiation, the resist
composition comprising: a film-forming polymer having
30 a carboxyl group in a side chain of a monomer unit,
the film-forming polymer further including an
additional acidic functional group in a side chain of
a monomer unit such that the additional acidic
functional group includes an acid-cleavable protective
35 group; and a photoacid generator that releases an acid
in response to a decomposition caused by an absorption
of the optical radiation used in the exposure process,

1 the resist film becoming soluble to the basic solution
upon a deprotection of the acid-cleavable protective
group from the side chain of the monomer, wherein the
carboxyl group contains a protective group represented
5 by a formula (I),



10 where n is an integer of 1 - 4, R is any of a hydrogen atom, an alkyl group, an alkoxy group, or an
alkoxycarbonyl group connected to an arbitrary
position excluding a third position that forms an
15 ester bonding.

The acid-sensitive polymer used for the base
resin of the resist composition of the present
invention includes various polymers ranging from
various copolymer compounds containing a monomer unit
20 that includes therein the foregoing lactone structure
and the additional acidic functional group attached to
the resist side chain and including the acid-cleavable
protective group, to a terpolymer including the
foregoing monomer unit and other arbitrary monomer
25 units.

It should be noted that the polymer used in
the present invention preferably contains at least one
monomer unit that contains the foregoing carboxyl
group including the protective group. The monomer
30 unit may be selected from any of acrylate monomer
unit, methacrylate monomer unit, vinylphenol monomer
unit, N-substitute maleimide monomer unit, and styrene
monomer unit. Alternatively, the monomer unit may be
the one that has an ester group including therein a
35 monocyclic alicyclic hydrocarbon. Monomer units that
includes a structure of adamantyl group or norbornyl
in the polycyclic alicyclic hydrocarbon part are most

1 preferable.

Further, it is preferred that the resist composition of the present invention shows an optical absorption, when used to form a resist film on an SiO_2 substrate, of 1.75 or less in the deep-ultraviolet wavelength band of 180 - 300 nm, which is used in the conventional exposure process. When the absorption is increased above the foregoing value, the transmittance of the resist film decreases substantially and the patterning becomes difficult.

In the acid-sensitive copolymer noted above, it is also preferable that a monomer unit, which causes a polymerization with the monomer unit that includes the carboxyl group in which the foregoing lactone protective group is included, includes another carboxyl group having the acid-cleavable protective group. Thus, the acid-sensitive copolymer of the present invention may include a monomer unit having a first carboxyl group that includes the foregoing lactone part as a first protective group and further a monomer unit having a second carboxyl group that includes the foregoing acid-cleavable protective group as a second protective group.

It should be noted that the foregoing monomer unit having the second carboxyl group preferably includes the carboxyl group such that the protective group causes a deprotection in response to the acid released by the photoacid generator, which may be added to a side chain of the same monomer unit, and that the protective group of the carboxyl group has a structure represented by the formula (II),

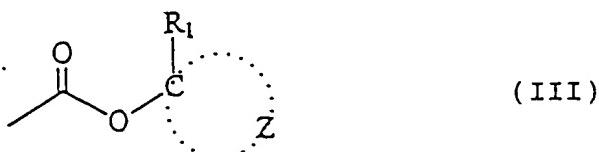
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1 wherein R_1 represents a substituted or unsubstituted
alkyl group and may have a straight chain or a
branched chain containing 1 - 4 carbon atoms, while Z
represents the atoms that are necessary to complete
5 the alicyclic hydrocarbon group together with the
carbon atoms attached to R_1 .

There are various forms possible for the
second carboxyl group, while the preferable form is
represented according to the formula (III) below,

10



15 wherein R_1 and Z are defined already in the formula
(II).

The preferred resist composition of the
present invention is supplied in a form of solution
dissolved into a solvent, which is selected from a
20 group of ethyl lactate, methylamylketone, methyl-3-
methoxypropionate, ethyl-3-ethoxypropionate,
propyleneglycolmethylether acetate and a mixture
thereof. The resist solution may further contain
butylacetate, τ (gamma)-butyrolactone, propyleneglycol
25 methylether and a mixture thereof as additional
solvent.

In another aspect of the present invention,
there is provided a method of forming a resist pattern
comprising the steps of:

30 coating a resist composition of the present
invention as set forth before on a substrate to form a
resist film;

exposing the resist film to an exposure
optical radiation that induces a decomposition of the
35 photoacid generator in the resist composition; and
developing the exposed area in a basic
solution.

1 Further, the present invention provides a
fabrication process of a semiconductor device
comprising the steps of:

coating a resist composition of the present
invention as set forth before on a substrate to form a
resist film;

exposing the resist film by an exposure optical radiation that induces a decomposition of the photoacid generator in the resist composition;

10 developing the resist film exposed to the
exposure optical radiation by a basic solution; and
etching the substrate while using the resist
pattern as a mask.

In the process of resist pattern formation or semiconductor device fabrication of the present invention as set forth above, it is further preferred to apply a heat treatment to the resist film formed on the substrate before and after the exposure process. In other words, the foregoing process may include a prebaking process and a post-exposure baking (PEB) process. The prebaking process and the PEB process may be conducted as commonly practiced in the art.

In the acid-sensitive copolymer of the present invention, it is preferred to set the proportion of the monomer unit, which has the lactone part represented by the formula (I) with respect to the total copolymer to fall in the range between 0.1 - 80 mol%, more preferably 10 - 50 mol%. When the proportion of the monomer unit becomes lower than about 10 mol%, the adhesion of the resist film to the substrate is impaired and the satisfactory patterning becomes difficult. When, on the other hand, the proportion exceeds 60 mol%, the formation of ultra-fine patterns becomes difficult due to the decrease of the monomer units that contains the acid-cleavable additional protective group. When the proportion exceeds 80 mol% in particular, the resin becomes

1 soluble to the basic solution before the exposure
process.

It is recommended to set the proportion of
the photoacid generator to fall in the range of 0.1 -
5 50 wt% with respect to the polymer weight, more
preferably to 1 - 15 wt%. Further, the weight average
molecular weight of the polymer used in the present
invention may fall in the range of 2,000 - 1,000,000,
more preferably the range of 5,000 - 50,000.

10 The additional solvent to be added to the
resist solution may not be necessary when the
solubility of the solutes is good. When the
solubility of the solutes is poor, on the other hand,
it is recommended to use such an additional solvent
15 with a proportion of 1 - 30 wt%, more preferably 10 -
20 wt%, with respect to the main solvent.

The basic solution used for the developer
may include an aqueous solution of a metal hydroxide
of group I or II metals such as KOH or an aqueous
20 solution of an organic base not containing a metal
ion, such as tetraalkylammonium hydroxide.
Particularly, the use of tetramethylammonium hydroxide
(TMAH) is preferred. Further, various additives such
as a surfactant may be added for improving the
25 efficiency of developing.

Other objects and further features of the
present invention will become apparent from the
following detailed description when read in
conjunction with the attached drawings.

30

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS.1A - 1F are diagrams showing the
fabrication process of a semiconductor device
according to an embodiment of the present invention.

35

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT
[GENERAL]

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1 The present invention relates to a chemical
amplification resist composition that forms a positive
resist pattern on a substrate upon a developing
process conducted by a basic aqueous solution.

5 The resist composition of the present
invention includes:

(a) an acid-sensitive film-forming polymer
insoluble to a basic aqueous solution and having a
carboxyl group on a side chain of a monomer unit that
10 constitutes the film-forming polymer, the carboxyl
group containing a protective group, the film-forming
polymer further having an additional acidic functional
group different from the carboxyl group on a side
chain of a monomer unit constituting the film-forming
15 polymer, the additional acidic functional group
containing an acid-cleavable protective group, which,
upon deprotection from the side chain, causes a change
in the film-forming polymer to become soluble to an
alkaline aqueous solution; and

20 (b) a PAG releasing an acid in response to an
optical exposure, which acid causing a deprotection of
the acid-cleavable protective groups, in response to a
decomposition caused in turn in response to an
absorption of an exposure optical radiation,

25 wherein the film-forming polymer contains a
lactone part represented by the formula (I) or (II) as
the protective group of the carboxyl group.

The protective groups release protonic acids
upon the deprotection, and the resist composition
30 achieves a high sensitivity as a result of the
chemical amplification thus occurred. After the
deprotection of the protective groups, the exposed
area in the resist film becomes soluble to alkalis,
and it becomes possible to form a positive resist
35 pattern from the resist film by conducting a
development process while using a basic solution for
the developer.

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1 It should be noted that the lactone
represented by the formula (I) shows a strong polarity
and further a weak solubility to alkalis. Thus, the
solubility of the exposed area in the resist film
5 after the deprotection of the acid-cleavable
protective group, is further enhanced. In the polymer
of the present invention, the pattern formation is
achieved by using the ^{polarity} change. Thus, the
resist pattern formed in the present invention is free
10 from swelling.

The structure of the acid-sensitive polymer
used in the resist composition of the present
invention as a base resin is not limited as long as
the foregoing requirement for the chemical
15 amplification mechanism is met. However, in view of
the demanded dry etching resistance of the resist,
which should be at least comparable with that of the
conventional Novolak resist, and further in
consideration of the fact that the resist should be
20 acid-sensitive, the use of a polymer including an
acrylate or methacrylate monomer unit that has a
polycyclic alicyclic hydrocarbon compound in an ester
group is recommended. Alternatively, the use of
comonomers to prepare copolymers such as a
25 vinylphenol, N-substituted maleimide or a styrene is
recommended. Particularly, the use of the acrylate or
methacrylate polymer is preferable in the exposure
process conducted by an optical radiation having a
wavelength of 250 nm or less, in view of reduced
30 optical absorption. In the exposure process conducted
by a deep ultraviolet radiation, it is generally
preferable to use a polymer that does not contain
benzene ring, which strongly absorbs the deep
ultraviolet radiation, or chromophore such as
35 conjugated double bond that shows a large molar
extinction coefficient.

In the case a deep ultraviolet optical

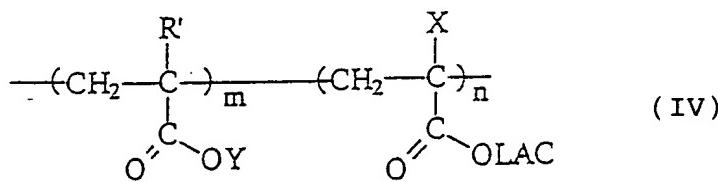
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1 source such as an ArF excimer laser is used for the
optical source, the transparency of the resist at the
wavelength of 193 nm becomes an especially important
factor in addition to the dry etching resistance. In
5 such a case, it is recommended to use a polymer,
particularly an acrylate or methacrylate polymer,
which contains a polycyclic alicyclic hydrocarbon
having a high dry etching resistance such as adamantyl
group or norbornyl group, in addition to the cleavable
10 ester group.

The foregoing acrylate or methacrylate
polymer as well as other acid-sensitive polymers may
have a wide range of molecular weight (weight-average
molecular weight, M_w), preferably in the range between
15 2,000 and 1,000,000, more preferably in the range
between 3,000 and 50,000.

In the case of using an acrylate or
methacrylate polymer, the formula of the polymer is
represented as

20



25 wherein R' represents a hydrogen atom or an arbitrary
substituent such as halogen, an alkyl group, a methyl
group, and the like; Y represents an arbitrary acid-
cleavable protective group such as tBu group, a
tetrahydropyranyl group, an isobornyl group, 2-methyl-
30 2-adamantyl group, and the like; m and n represent a
normalized mole ratio of each monomer unit ($m + n = 1$);
X represents, when not specified otherwise, a hydrogen
atom, a halogen atom such as Cl or Br, a lower grade
alkyl group such as a methyl group or ethyl group, or
35 a cyano group; and LAC represents the lactone part of
the formula (I).

The acrylate or methacrylate polymer of the

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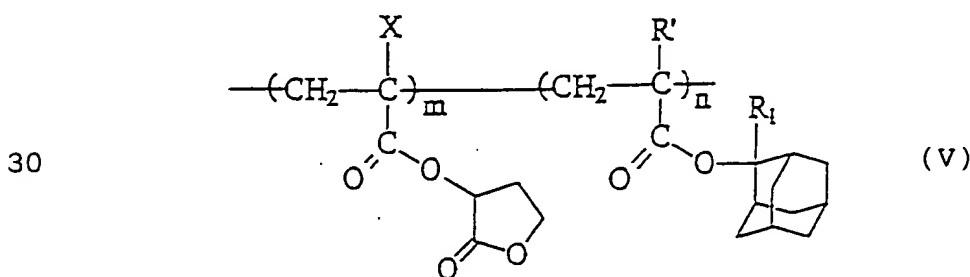
1 present invention can be easily synthesized by a
commonly used polymerization process. For example,
the polymer may be formed advantageously by heating
monomers in the presence of AIBN (2, 2'-
5 ~~azobisisobutyronitrile~~
~~azobisisobutyronitrile~~) which is used commonly for a
free radial initiator. Further, the acid-sensitive
polymers other than the foregoing acrylate or
methacrylate polymer may be prepared according to a
well established process.

10 In the resist composition of the present
invention as a base resin, it is preferable to use a
monomer unit having the structure of the formula (II)
for the protective group of the acidic functional
group.

15 While there are various possible forms for
the protected acidic functional groups, it is
preferable to use a compound having the formula (III)
for this purpose.

20 In more detail, the copolymer formed of the
monomer units that have a carboxyl group containing
therein a protective group, is represented by a
formula (V). More specifically, the acid-sensitive
polymer may be formed of the copolymer represented by
the formula (V) as

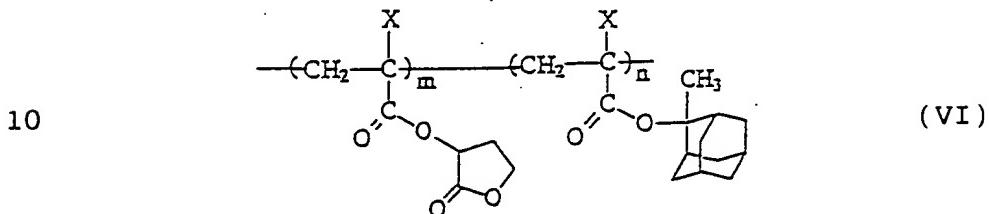
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35 wherein R₁, R', X, m and n are already defined, the
substituent R' and X may be identical or different and
preferably formed of a hydrogen atom or a methyl

1 group.

In implementing the present invention, it is advantageous to use a τ (gamma)-butyrolactone-2-yl methacrylate/2-methyl-2-adamantyl methacrylate copolymer represented by the formula (VI)



15 for the acid-sensitive copolymer, wherein X represent a methyl group or a hydrogen atom and may be the same or may be different ^{from} each other.

The resist composition containing such a copolymer or other polycyclic alicyclic ester shows a high dry etching resistance (RIE resistance). In order to achieve an RIE resistance of the commonly used Novolak resin, it is necessary to set the content of the 2-methyl-2-adamantyl methacrylate, which forms the second monomer unit in the copolymer, to about 50 mol %. As the copolymer does not contain a conjugate double bond or benzene ring in the structure, the copolymer is transparent to the optical radiation of 193 nm wavelength produced by an ArF excimer laser.

In the foregoing copolymer, it is preferable to set the proportion of the τ -butyrolactone-2-yl methacrylate forming the first monomer unit of the copolymer to 20 - 70 mol%, more preferably to 30 - 60 mol%. When the proportion of the foregoing monomer unit is reduced below about 20 mol%, there appears a tendency that the resist pattern peels off. When, on the other hand, the proportion of the monomer unit exceeds about 80 mol%, the resin becomes soluble to a

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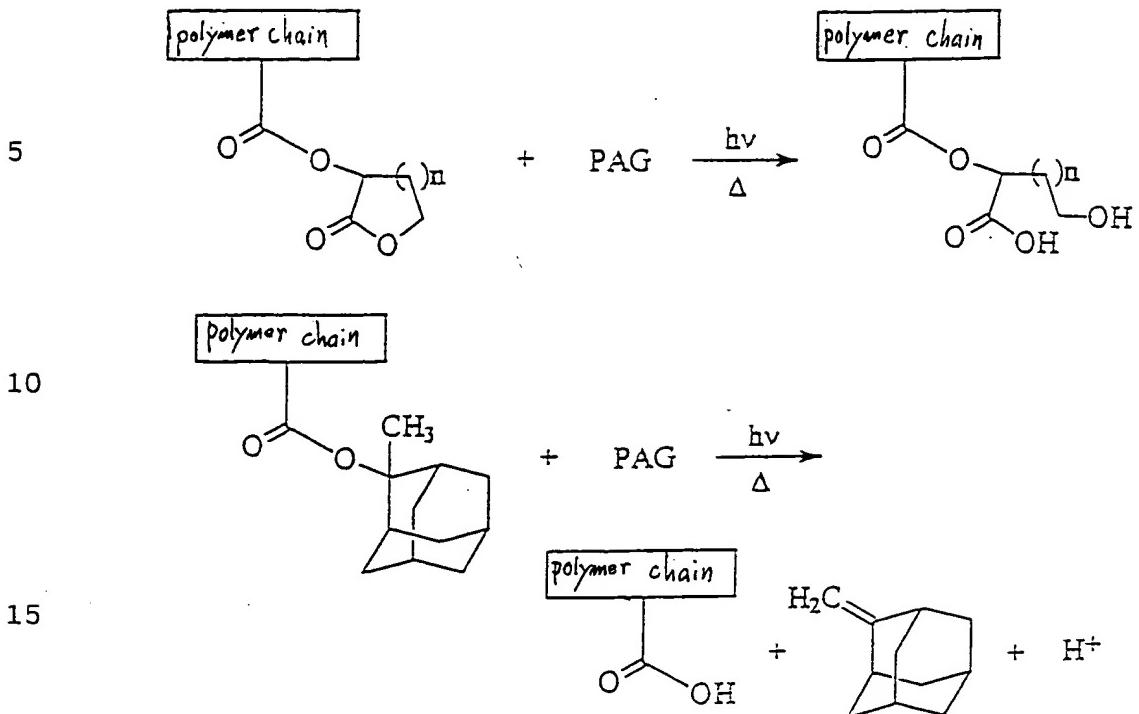
1 basic aqueous solution. Most preferably, the monomer
unit is contained with a proportion of 40 - 60 mol%.

5 It should be noted that the mechanism of the
chemical amplification process for the foregoing
copolymer resist is identical to that of a general
chemical amplification process. The copolymer further
has an advantageous effect of solubility to alkalis
provided by the lactone group in the monomer unit.

10 It is well known that a polymer of acrylate
or methacrylate shows a high transparency in the deep
ultraviolet wavelength band. As the copolymer
represented by the formula (VI) does not contain a
chromophore showing a large molar extinction
coefficient in the wavelength band of 190 - 250 nm in
15 the two ester parts thereof, it is possible to obtain
a high sensitivity resist composition applicable to a
deep ultraviolet exposure process from the foregoing
copolymer, by adding a suitable amount of PAG.

20 When the foregoing polymer is used for the
base resin of a resist film, there proceed following
reactions in the exposed part of the resist
simultaneously or separately, by consuming a small
amount of H₂O contained in the resist film. Thereby,
the reaction stops when H₂O in the exposed region ~~is~~^{is}
25 consumed. As a protonic acid is regenerated after the
deprotection of the adamantyl group, the resist film
shows a very high sensitivity.

1



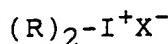
20 In the combination as represented by the foregoing copolymer, there is induced deprotection reaction that regenerates the protonic acid as a result of the exposure process, and the resist film shows a very high sensitivity. After the deprotection of the protected group, a carboxylic acid is generated. As the other lactone part is also soluble to alkalis, the exposed part of the resist film changes to be soluble to a basic aqueous solution. Thus, by applying a developing process conducted in a 30 basic aqueous solution, a positive pattern is obtained in which the exposed part is dissolved. As such a developing process employs a change of the polarity occurring in the resist film, the pattern thus formed is substantially free from swelling.

35 In the chemical amplification resist of the present invention, it should be noted that it is possible to use a conventional PAG used in a chemical

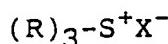
1 amplification resist for radiation sources such as far
ultraviolet, vacuum ultraviolet or X-rays. While not
limited, the PAG for use in the present invention
includes the following:

5

(I) onium salts having a formula



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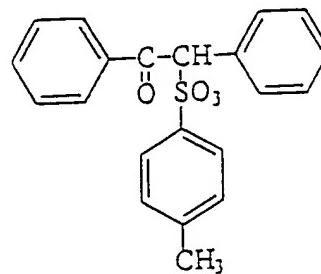
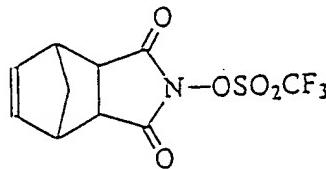


wherein R represents a substitutional or non-
substitutional benzene ring or alicyclic group, while
X represents BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , $CF_3SI_3^-$, ClO_4^- , and
15 the like.

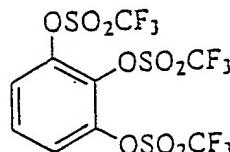
(II) sulfonic acid ester

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25



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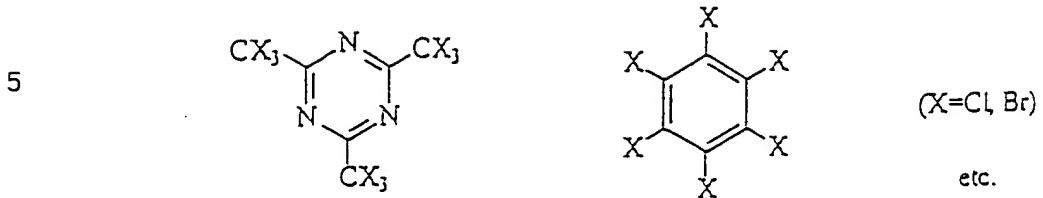


etc.

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1 (III) halides



10 The PAG noted above may be used in the
resist composition of the present invention with
various proportions. A proportion of 0.1 - 50 wt%
(with respect to the polymer weight), more preferably
1 - 15 wt%, is recommended. In the case of the resist
composition of the present invention, it is ~~preferably~~
15 to adjust the structure of the polymer as well as the
structure and proportion of the PAG such that the
resist film shows an ~~absorbance~~ ^{absorbance} of 1.75 or less.

20 It should be noted that the resist
composition of the present invention is advantageously
used in the form of a resist solution in which the
foregoing acid-sensitive polymer and the PAG are
dissolved into an organic solvent. The organic
solvent may be selected, although not limited, from:
25 ethyl lactate, methylamylketone, methyl-3-
methoxypropionate, ethyl-3-ethoxypropionate, and
propyleneglycolmethyleneether acetate. Further, two or
more solvents may be mixed. While the proportion of
the solvent with regard to the polymer is not limited,
30 it is preferable to optimize the proportion such that
a suitable viscosity for a successful spin coating
process is obtained.

The resist solution thus formed may further contain an additional, auxiliary solvent. Such an auxiliary solvent is not necessary when the resist film is formed uniformly as a result of the spin coating process. On the other hand, when the

1 uniformity of the coated resist film is poor, the
2 quality of the resist film can be improved by adding
3 such an auxiliary solvent to the foregoing primary
4 solvent generally within the proportion of 1 - 30 wt%,
5 more preferably 10 - 20 wt%. For the auxiliary
solvent, a solvent selected from butyl acetate,
 τ (gamma)-butyrolactone, propyleneglycol methylether,
and the like may be used.

The present invention further provides a
10 process of forming a positive resist pattern on a
substrate by using the foregoing resist composition.
The formation of the resist pattern can be achieved as
follows.

First, a resist film is formed using the
15 resist composition of the present invention on a
substrate. The substrate may be a substrate used
commonly in the fabrication of semiconductor devices,
or the like, and includes a Si substrate, a glass
substrate, a non-magnetic ceramic substrate, and the
20 like. The substrate may carry thereon various
additional layers such as a SiO_2 film, metal
interconnection layer, interlayer insulation film,
magnetic layer, and the like. Further, the substrate
may carry thereon various interconnection patterns and
25 circuit patterns. Further, the substrate may be the
one that has been subjected to a hydrophobic
processing for improving the adhesion of the resist
film. Such a hydrophobic processing may be conducted
according to the well established process that uses
30 1,1,1,3,3,3-hexamethyl disilazane (HMDS).

The application of the resist composition is
achieved by merely applying the resist solution
directly on the substrate according to a commonly
practiced process such as a spin-coating process, a
35 rolling process, a dipping process, and the like.
Among others, the spin-coating process is most
convenient, and the resist film may be formed with a

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- 1 thickness of 0.1 - 200 μm . In the case of the
a exposure process conducted ~~using~~ by a KrF or an ArF
excimer laser, it is preferable to set the thickness
of the resist film in the range of 0.1 - 5 μm .
5 Further, the thickness of the resist film can be
changed as necessary, depending on the particular
application of the resist.

The resist film thus formed on the substrate
is subjected to a prebaking process before exposing
10 the resist film to the exposure radiation. The
prebaking process is preferably conducted at a
temperature of 60 - 180°C for a duration of 30 - 120
seconds. Such a prebaking process can be achieved by
15 using the heating means that is used commonly in the
resist process. For example, the prebaking process
may be conducted by using a hot plate, an infrared
oven, or a microwave oven.

After the prebaking process, the resist film
is exposed in an exposure system. The exposure system
a 20 may ^{be} any of optical exposure systems including far
ultraviolet and deep ultraviolet exposure system, an
X-ray exposure system, an electron beam exposure
system, and the like. In the resist composition of
the present invention, it is particularly advantageous
25 to use a KrF excimer laser with the wavelength of 248
nm or an ArF excimer laser with the wavelength of 193
nm. In the description of the present invention,
however, it should be noted that the phrase
"radiation" encompasses any radiation produced by any
30 radiation source noted above.

After the exposure process, the resist film
is subjected to a PEB process, to induce a
deprotection reaction of the protective group, while
using the protonic acid as a catalyst. The PEB
35 process can be achieved just like the prebaking
process as long as the heat treatment is conducted
within the range in which the deprotection reaction

1 proceeds sufficiently. For example, the PEB process
may be conducted at the temperature of 60 - 180°C for
30 - 120 seconds. The condition of the PEB process
may be adjusted depending on the desired pattern size,
5 pattern profile, and the like.

After the PEB process, the resist film is developed in a basic aqueous solution. The basic aqueous solution may be applied to the resist film as a developer by using a developing apparatus, which may be any of a spin developer, a dip developer or a spray developer. The developer may be any of an aqueous solution of a Group I or Group II metal element or an aqueous solution of an organic salt free from a metal ion such as tetraalkylammonium hydroxide, wherein it is particularly preferable to use an aqueous solution of tetramethylammonium hydroxide (TMAH) that does not contain a metal element. In order to improve the efficiency of developing, it is also possible to add various additives to the developer such as a surfactant.

As a result of such a developing process, the exposed area of the resist is dissolved, and the unexposed area of the resist remains as a resist pattern.

25 Hereinafter, various embodiments of the
present invention will be described with regard to the
synthesis of the acid-sensitive polymer, preparation
of the resist composition and formation of the resist
pattern. The embodiments below, however, are only
30 examples and the present invention is by no means
limited to these specific embodiments.

[FIRST EMBODIMENT]

SYNTHESIS OF τ -BUTYROLACTONE-2-YL METHACRYLATE

35 A three-neck flask of 200 ml size is dried thoroughly and filled with N₂, after connecting thereto a dropping funnel, a calcium chloride tube and

1 a N₂ supply tube at respective necks. Next, 50 ml of
dry methylene chloride, 5.0g (48.9 mmol) of 2-hydroxy-
 τ (gamma)-butyrolactone, and 5.45g (53.9 mmol) of dry
triethylamine are introduced into the three-neck flask
5 and stirred in an N₂ atmosphere at 0°C by using a
teflon-coated stirrer bar.

Next, 5.11g (48.9 mmol) of methacryloyl
chloride previously held in the dropping funnel is
introduced by a dropping process conducted for 1 hour,
10 and the liquid thus obtained is stirred at a room
temperature for 2 hours. The resultant solution is
then taken into a separating funnel of a 300 ml size,
and the solution thus taken is washed with 100 ml of
water, followed by washing with a saturated sodium
15 chloride water. Thereby, the water layer is extracted
three times with methylene chloride, and the extracts
are added to the organic layer. The organic layer
thus collected is then dried over anhydrous sodium
sulfate, and filtered through a filter paper. As a
20 result of the filtering, a brownish oil is obtained,
and the brownish oil is purified by a silica gel
column chromatography. As a result of the
purification, a colorless transparent oil is obtained
as a target product.

25

yield 7.25g (78.1%)

¹H NMR(CDCL₃, d, J in Hertz): 1.98(3H,s), 2.35(1H,m),
2.76(1H,m), 4.35(1H,m), 4.51(1H,m), 5.43(1H,t,J=6.5),
5.70(1H,s), 6.22(1H,s), wherein s in the bracket
30 represents singlet, d represents doublet and m
represents multiple.

[SECOND EMBODIMENT]

SYNTHESIS OF A COPOLYMER OF τ -BUTYROLACTONE-2-YL
35 METHACRYLATE AND 2-METHYL-2-ADAMANTYL METHACRYLATE

A flask of 100 ml size is used to hold 3g
(17.6 mmol) of τ (gamma)-butyrolactone-2-yl

1 methacrylate, 3.51g (14.4 mmol) of 2-methyl-2-
adamantyl methacrylate, 788mg (4.8mmol) of AIBN (15
mol%) and 10.7 ml of dioxane, together with a magnetic
stirrer bar, and the mixture in the flask is stirred
5 by using the magnetic stirrer bar in a dry N₂
environment at a temperature of 70°C for 8 hours. A
resultant viscous fluid is added dropwise in 800 ml of
methanol, to form a precipitate.

Next, the precipitate is filtered by using a
10 glass filter and the resin thus filtered is dried in a
vacuum oven at 45°C for 6 hours. The resin thus
obtained is then dissolved into THF. After repeating
the precipitation purification twice by using
methanol, the resin is dried in the vacuum oven at
15 45°C for 18 hours. As a result, a whitish resin ^{powder} ~~power~~
is obtained with a yield of 5.35g (82.2%).

By conducting a ¹HNMR analysis, it was
confirmed that the resin contains lactone and
adamantyl with a ratio of 51: 49.
20 Mw:14,900, Mw/Mn=1.83 (in terms of standard
polystyrene)

The result of an IR analysis was as follows.
IR(KRS-5, cm⁻¹): 2913, 1791, 1737, 1261,
1147, 1103
25

[THIRD EMBODIMENT]
RESIST PATTERN FORMATION

The copolymer synthesized in the second
embodiment is dissolved into PGMEA (propyleneglycol
30 methylether acetate) to form a 15 wt% solution. The
solution is further added with 8 wt% τ (gamma)-
butyrolactone as the auxiliary solvent. The solution
thus obtained is further added with 2 wt% of
triphenylsulfonium trifluorosulfonate for complete
dissolution.
35

The resist solution thus obtained is then
filtered by a teflon membrane filter of 0.2 μ m size

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1 and spun~~y~~ onto a Si substrate processed by HMDS, to
form a resist film. The resist film thus formed is
subjected to a prebaking process at 120°C for 60
seconds, and a resist film having a thickness of 0.7
5 µm.

The resist film thus obtained is then
subjected to an exposure process, in which the
exposure process is conducted by a KrF excimer laser
stepper having a numerical aperture of 0.45.

10 After the exposure, the resist film is
subjected to a PEB process at a temperature of 110°C
for 60 seconds, and a resist pattern is developed by
applying a 2.38% TMAH (tetramethyl ammonium
hydroxide) developer. After the development, the
15 resist pattern was rinsed by a deionized water.

It was confirmed that, as a result of the
exposure conducted with a dose of 30.0 mJ/cm², a line-
and-space pattern of 0.25 µm pitch is successfully
resolved.

20

[FOURTH EMBODIMENT]

RESIST PATTERN FORMATION

25 The resist solution of the third embodiment
is applied on a hydrophobic Si substrate surface
processed by HMDS, similarly to the case of the third
embodiment, to form a resist film with a thickness of
0.4 µm. The resist film is then subjected to an
exposure process conducted by using an ArF excimer
laser stepper having a numerical aperture (NA) of
30 0.55. After the exposure, the resist film is
subjected to a PEB process conducted at 100°C for 60
seconds, followed by a developing process using a
2.38% TMAH developer, to form a resist pattern. The
resist pattern thus formed is rinsed by a deionized
35 water.

According to the experiment of the present
embodiment, it was confirmed that a line-and-space

1 pattern of 0.20 μm pitch is successfully resolved when
an exposure dose of 26 mJ/cm^2 is used.

[FIFTH EMBODIMENT]

5 FORMATION OF A RESIST PATTERN

The copolymer synthesized in the foregoing second embodiment is dissolved to form a 15wt% PGMEA solution, and a resist solution is formed by adding 2 wt% of diphenyliodonium trifluoromethanesulfonate with respect to the resin, to the foregoing PGMEA solution. The resist solution thus obtained is applied on a surface of a Si substrate processed by HMDS by a spin coating process. After a prebaking process conducted at 120°C for 60 seconds, a resist film having a thickness of 0.4 μm is obtained.

The resist film is then subjected to an exposure process in an ArF exposure system, followed by a PEB process conducted at 100°C for 60 seconds. The resist film thus exposed is then developed by a 2.38% TMAH developer, and rinsed by a deionized water.

According to the present embodiment, it was confirmed that a line-and-space pattern of 0.20 μm pitch is successfully resolved when an exposure dose of 20 mJ/cm^2 is used.

25

[SIXTH EMBODIMENT]

SYNTHESIS OF A COPOLYMER OF τ (gamma)-BUTYROLACTONE-2-YL METHACRYLATE AND ISOBORNYL METHACRYLATE

A flask of 100 ml size is used to hold 5.0g (29.4 mmol) of τ -butyrolactone-2-yl methacrylate, 6.54g (29.4 mmol) of isobornyl methacrylate, 19.6 ml of dioxane and 1.44g (8.8 mmol) of azobisisobutyronitrile (AIBN), together with a teflon-coated stirrer bar, and the mixture in the flask is stirred by using the stirrer bar in an N_2 environment at a temperature of 70°C for 8 hours. A resultant fluid is diluted by THF and added dropwise into 1 l of

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1 methanol containing a small amount of ~~hydroquinone~~, to
form a precipitate.

5 Next, the precipitate thus formed is filtered by using a glass filter and dried under a 0.1 mmHg pressure at 45°C for 16 hours. The resin thus obtained is then dissolved again into THF, and the foregoing filtering and drying process are repeated twice. As a result of the foregoing process, a whitish resin ~~powder~~ is obtained.

10 By conducting a ^1H NMR analysis, it was confirmed that the resin contains lactone and isobornyl with a ratio of 49: 51. The copolymer thus obtained shows a transmittance of 96% at 248 nm and a transmittance of 65% at 193 nm, provided that the 15 polymer film is formed on an SiO_2 substrate with a thickness of 1 μm .

yield 8.61g (80%)
Mw:15,400 (in terms of standard polystyrene)
20 dispersion 1.82
 $\text{IR}(\text{KRS-5, cm}^{-1})$: 2961, 1792, 1736, 1250,
1163, 1102

[SEVENTH EMBODIMENT]

25 FORMATION OF RESIST PATTERN

The copolymer synthesized in the previous sixth embodiment is dissolved to form a 145 wt% PGMEA solution. Further, a resist is formed by adding 2 wt% of triphenylsulfonium trifluoromethanesulfonate with 30 respect to the resin, to the foregoing PGMEA solution. The solution further contains 6 wt% of $\tau(\text{gamma})$ -butyrolactone as an auxiliary solvent.

The resist solution thus obtained is then applied on a surface of a Si substrate processed by 35 HMDS and subjected to a prebaking process conducted at 120°C for 60 seconds. Thereby, a resist film having a thickness of 0.4 μm is formed.

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1 The resist film is then subjected to an
exposure process conducted by an ArF excimer laser
exposure system, followed by a PEB process conducted
at 100°C for 60 seconds. After a developing process
5 conducted by a 2.38% TMAH developer, followed by a
rinse process conducted by a deionized water, a line-
and-space pattern of 0.20 μm pitch is successfully
resolved by using an exposure dose of 32 mJ/cm².

10 FIGS.1A - 1F show a fabrication process of a
semiconductor device conducted by a resist composition
of the present invention.

Referring to FIG.1A, a gate oxide film 2 is
formed on a surface of a Si substrate, and a
15 polysilicon layer 3 is deposited thereon by a CVD
process. The polysilicon layer 3 thus formed is given
a conductivity by introducing thereinto an n-type
impurity element such as P. After the formation of
the polysilicon layer 3, a WSi film 4 is formed
20 further thereon by a sputtering process or a CVD
process.

Next, in the step of FIG.1B, the resist
composition of any of the foregoing embodiments is
applied on the structure of FIG.1A, to form a resist
25 film. The resist film thus formed is first subjected
to a prebaking process and further subjected to an
exposure process conducted by a KrF excimer laser
exposure system. After the exposure, the resist film
is subjected to a PEB process, followed by a
30 developing process conducted by using an alkaline
developing liquid. As a result of the developing
process, a resist pattern 5 having a minimum pattern
width of 0.25 μm is successfully formed.

By using the resist pattern 5 thus formed as
35 a mask, the WSi layer 4 and the polysilicon layer 5
underneath are etched successively to form a gate
electrode.

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1 Next, an ion implantation process is
conducted while using the gate electrode as a mask, to
form a N⁻-type diffusion region 6 in the substrate 1.

5 Next, in the step of FIG.1C, the resist
pattern is removed and an SiO₂ film 7 is formed on the
entire surface of the structure of FIG.1B by a CVD
process.

10 The SiO₂ film 7 is then subjected to an
anisotropic etching process acting generally
perpendicularly to the principal surface of the
substrate 1 in the step of FIG.1D, to form a side wall
insulation film 8. Further, an ion implantation
process is conducted while using the gate electrode
and the side wall insulation film as a mask, to form
15 N⁺-type diffusion region 9 in the substrate 1.

20 The N⁺-type diffusion region 9 thus formed
is then activated in the step of FIG.1E by conducting
a thermal annealing process in an N₂ atmosphere,
followed by a thermal oxidation process to form an
oxide film 10 on the exposed surface of the diffusion
region 9.

25 Further, in the step of FIG.1F, an
interlayer insulation film 11 is deposited on the
structure of FIG.1E and a resist film of the present
invention is applied on the interlayer insulation film
11 thus formed.

30 After a prebaking process of the resist
film, an exposure process for exposing a contact hole
corresponding to the gate electrode is conducted by
using an ArF excimer laser exposure system. After a
PEB process, the resist film is subjected to a
developing process conducted by using an alkaline
developing liquid, and a minute contact hole having a
diameter of 0.20 μm is successfully obtained.
35 Further, the resist pattern is removed, and an Al
wiring pattern 12 is provided on the interlayer
insulation film 11 in contact with the gate electrode

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1 through the contact hole thus formed.

In the present invention, it should be noted
that the resist film, containing alicyclic ester group
5 which has a small optical absorption to a short
wavelength optical radiation and a high dry-etching
resistance, shows simultaneously a strong adhesion to
the underlying layer 4 due to the existence of the
lactone part that has a large dipole moment.

10 In the resist composition of the present
invention, the lactone part is formed from a low cost
source of 2-hydroxy- τ (gamma)-butyrolactone. Further,
the resist composition can be formed with a higher
synthetic yield than in the case in which mevalonic
15 lactone is used. As demonstrated in the experiments
described before, it should be noted that the monomers
and copolymer are synthesized in the present invention
with a yield exceeding 80%.

Further, the present invention is not
20 limited to the embodiments described heretofore, but
various variations and modifications may be made
without departing from the scope of the invention.

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